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Bio-diesel Production from Residual Sunflower Oil by Trans-esterification (Acidic, Alkaline Enzymatic) and Analysis of Some of Its Physico-chemical Parameters

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Authors' contributions

This work was carried out in collaboration between both authors. Author STG designed the study and wrote the protocol. Author DK performed the study. Authors STG and DK managed the analyses of the study, wrote the first draft of the manuscript and literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: Recycling of residual sunflower oil for bio-diesel production, determination, and comparison with some of the physico-chemical parameters with the jatropha bio-diesel and ASTM D6751 and EN 14214 standards.

Study Design: Experimental observation with production of bio-diesel and characterization of some analytical parameters.

Place and Duration of the Study: Department of Microbiology and Biotechnology, Jnana Barathi Campus, Bangalore University, Bengaluru 560056, July 2015 to June 2016, India.

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Methodology: Acidic, Alkaline and Enzymatic trans-esterification was carried out with the residual sunflower oil for bio-diesel production by using the catalysts: HCl, NaOH and immobilized lipase enzyme (Hi-media RM1265) respectively. Some physico-chemical parameters of bio-diesel obtained in these processes were compared with the jatropha bio-diesel and ASTM, EN standards. The efficiency of the bio-diesel of the residual sunflower oil was analyzed by Fourier transform infrared spectroscopy technique (FTIR).

Results: The bio-diesel produced from residual sunflower oil by three different processes was analyzed for physico-chemical parameters: Density, Viscosity, Acid value, Cetane number, Iodine value and Flash point. By comparing these parameters with referral jatropha bio-diesel and ASTM D6751, PS121, EN 14214. The Cetane number (CN) responsible for auto-ignition of the sunflower bio-diesel was found to be more than 50 CN when compared with the jatropha bio-diesel (CN=47-50). The efficiency of the bio-diesel was assessed by using Fourier transform infrared spectroscopy technique. This showed that alkaline method was more effective when compared to the acidic and enzymatic methods in terms of more fatty acid ester formation.

Conclusion: The study parameters of produced bio-diesel from residual sunflower oil evinced suitability for recycling purpose. Alkaline trans-esterification method for bio-diesel production was cost effective and efficient as per Fatty Acid Methyl esters content (FAMES). Hence, it lays a foundation for the further research to utilize residual sunflower oil as an alternative fuel.

Keywords: Sunflower; bio-diesel; jatropha; cetane number; lipase; flash point.

1. INTRODUCTION

The coal and petroleum are non-renewable fossil fuels of nature and are used abundantly all over the world. Hence, are accepted as unsustainable due to the depleting resources. The extensive use of fuels in automobiles has led to the accumulation of carbon dioxide – greenhouse gases. The concentration of the carbon dioxide has exceeded the safer level of 350 ppm and reached dangerous levels of 450 ppm, which contributes significantly to the global warming. To overcome these problems, in recent years bio-fuel has drawn an attention as a sustainable energy source that may cope up as an alternative fuel [1-2].

Bio-fuels are the major alternative sources of energy accounting for more than 90% of the energy consumption in poor developing countries [2]. Several public institutions, state bio-fuel boards, state agricultural universities and cooperative sectors are also supporting the bio-fuel mission in different capacities. Bio-fuels include bio-ethanol, bio-methanol, bio-diesel, bio-gas, biosynthetic gas (bio-syngas), bio oil, bio-char and bio-hydrogen. The traditional way of production of bio-fuels was ethanol from corn, wheat, sugar beets or of cane and bio-diesel from vegetable oils. The fatty acid content of edible and non-edible oils is suitable for the production of bio-diesel as they minimize the release of carbon monoxide, nitrogen oxide, and sulfur to the environment hence gaining popularity. The utilization of waste vegetable oils

for bio-diesel production by trans-esterification process is one of the great environmental concern as they reduce the health hazards in human beings [3].

Several investigations are intended to re-consideration of non-edible oils and used vegetable oil from catering industries for bio-diesel production. The various properties associated with them are measured to find out the utility by comparing with reference of conventional jatropha bio-diesel [4].

Bio-diesel from sunflower oil has minimal impact on the domestic use of sunflower oil provided that the crop is grown commercially for use in both applications. There are few research reports available about the usage of sunflower oil as an alternate option as a blend with petro-diesel in suitable proportions [5]. Bio-diesel production from sunflower oil using calcium oxide [6-7], sunflower oil subjected to the trans-esterification with calcium oxide in supercritical methanol for obtaining bio-diesel [8] and also sunflower oil subjected for bio-diesel production using industrially important lipase enzyme from *Candida antarctica* are known [9-10].

Similarly, few reports are also available on the usage of used sunflower oil for bio-diesel production where they reported on the acid number, viscosity and phosphorus content [11] and production by using immobilized lipase enzyme as catalyst [12].

2.5 Enzymatic Trans-esterification

The enzymatic trans-esterification of the residual oil was carried out on incubator shaker at 200 rpm for a period of 48 hours at 40°C. 10 mL of the residual oil was taken in Erlenmeyer flask, 13.33 mL of ethanol fraction (1:4 of oil to ethanol) was added every one third of the reaction time. Once the first fraction of ethanol was added 400 mg of the immobilized lipase was added. After the addition of the last fraction of the ethanol, 0.6 mL of n-hexane was added and allowed for the reaction to take place in an incubator shaker, the reaction mixture was separated using separating funnel. Top most layer containing methylesters as bio-diesel and bottom layer as glycerol was separated. The obtained bio-diesel was subjected for FTIR analysis and physico-chemical parameters were determined by comparing it with referral jatropha, ASTM and EN standards [18].

2.6 Analytical Characterization of Bio-diesel Produced

The saponification process was carried out to determine the presence of free and combined fatty acids present in the oil [19]. The other physico-chemical parameters include measurement of Density by pycnometer and viscosity by viscometer at 24°C which is used to measure the internal fluid friction responsible for injector lubrication. Determination of saponification value for the measure the presence of combined and free fatty acid content at 24°C by titrimetric method [20]. Estimation of acid value gives the measure of number of carboxylic groups in a chemical compound which was measured by titrimetric method against known concentration of potassium hydroxide (KOH) using phenolphthalein as an indicator. Acid value should be lower than 0.50 mg KOH/g since the FFA produced might corrode the automotive parts which cause damage to vehicle engines and fuel tanks [21]. Iodine value is often used to determine the amount of unsaturation in fatty acids by Hannus reaction using titrimetric method [22-23]. Higher iodine value represents more C=C bonds. And cetane number (Hexadecane number) represents inverse function of fuel ignition delay. It indicates the ignition properties of the diesel. Higher cetane number indicates that fuel have shorter ignition delay periods, than the fuels having lower cetane number. Flash point is the minimum temperature of bio-diesel at which it ignites and determines the fuel efficiency measured by Pensky-martens

flash point apparatus. Cetane number is the readiness of the fuel to auto-ignite when injected into engine, measured by Near infra-red analyzer method adopted by analytical laboratory Bengaluru.

Ester content: FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a bio-diesel spectral resolution data over a wide spectral range analyzed for Fatty acid methyl ester. FTIR analysis was done in department of organic chemistry central college using BRUKER FTIR (model name: IFS 125HR).

3. RESULTS AND DISCUSSION

3.1 Comparative Results on Physico-Chemical Properties of Bio-Diesel with the Standards

The free and combined fatty acid content of the residual sunflower oil was determined for saponification value and found to be 192 mg KOH/g in residual sunflower oil and 197 mg KOH/g in jatropha oil. The bio-diesel obtained from residual sunflower oil had its efficiency checked to be used as an alternative bio-fuel after trans-esterification. The physico-chemical parameters were determined and compared with referral Jatropha bio-diesel and ASTM D6751-PS121 and EN standards [24].

In order to be used as bio-diesel, the physico-chemical parameters (Table 1) of the obtained trans-esterified bio-diesel must comply with a series of ASTM and EN standards. The viscosity responsible for the operation of the fuel injection equipment and injector lubrication [25-26], Iodine value for evaluating degree of unsaturation that determine the stability to oxidation in the bio-diesel [27-28], acid value represents free fatty acids was also determined to check the acid moieties in the bio-diesel [29], were measured. Cetane number for combustion efficiency was analyzed to check for the delay period in the bio-diesel, flash point was determined to know the fuel efficiency in terms of flammable vapors which can be ignited in air by a flame above its surface. By the comparative study of the above methods parameters, the unique observation was found to be the Cetane number showing more than 50 CN whereas standard jatropha showed 40-50. The bio-diesel obtained from alkaline method was found to have higher efficiency when compared with the referral jatropha bio-diesel and ASTM and EN standards thus, can be used as alternative source of bio-

diesel. Also the alkaline base used in the trans-esterification acts as catalyst but not reactants hence alkaline used is not consumed by trans-esterification reaction. And also the reaction did not take place at elevated temperature minimizes the soap formation, therefore alkaline trans-esterification is sustainable and stays the best method for bio-diesel production. Whereas bio-

diesel obtained from enzymatic method was found to have good efficiency when compared, but requires longer duration and is exorbitant to be used as alternative fuel. Whereas, the bio-diesel obtained from acidic method showed variation in some physico-chemical parameters and was found to be not efficient when compared with the standards (Figs. 2-4).

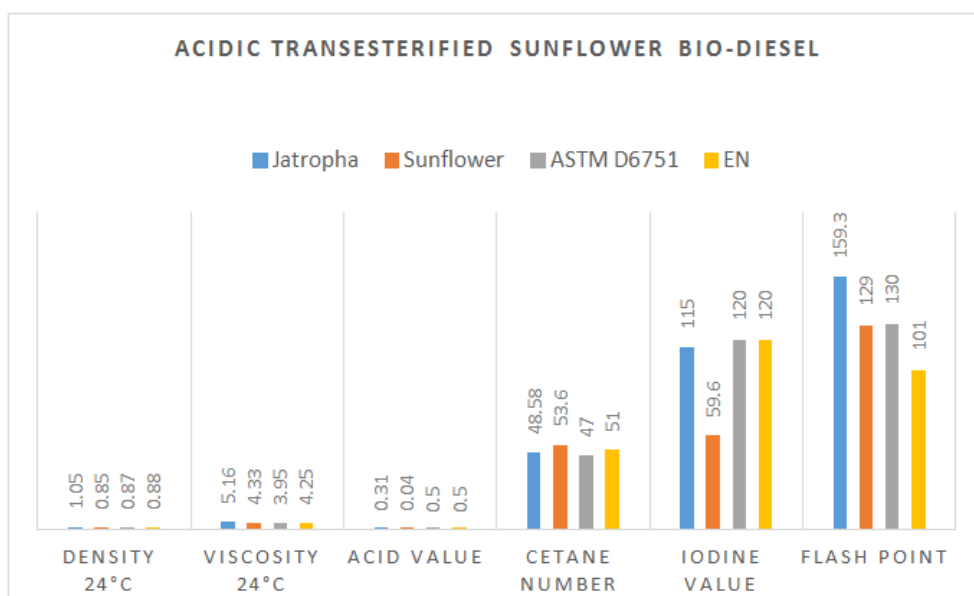


Fig. 2. Physico-chemical properties of sunflower bio-diesel produced by acidic trans-esterification, in comparison with jatropha bio-diesel, EN and ASTM standards

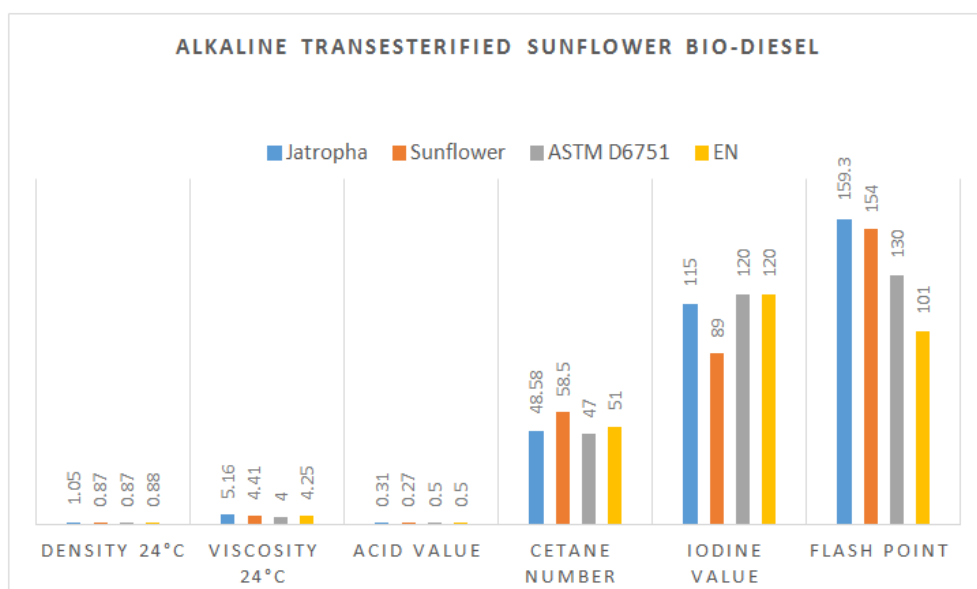


Fig. 3. Physico-chemical properties of sunflower bio-diesel produced by alkaline trans-esterification, in comparison with jatropha bio-diesel, EN and ASTM standards

Table 1. Physico-chemical properties of the sunflower residual oil bio-diesel, with comparative standards

Parameters	Comparative standards (ASTM D6751*/ ASTM PS121 **)	Bio-diesel produced by trans-esterification				
		European Standards 14214	Jatropha standards	Acidic method Sunflower	Alkaline method Sunflower	Enzymatic method Sunflower
Density 24°C (g/cc)	0.87**	0.86-0.90	1.05	0.85	0.87	0.94
Viscosity 24°C (mm ² /sec)	1.9-6*	3.5-5.0	5.16	4.33	4.41	5.66
Acid value (mg KOH/g)	Max 0.50*	0.5	0.31	0.04	0.27	0.33
Cetane number	Min 47*	51	48.58	53.6	58.5	58.3
Iodine value (g/100 g)	Max 120*	120	115	59.6	89	138
Flash point (°C)	Min 130*	101	159.3	129	154	130

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis (Figs. 5-8) was carried out to check the presence of FAMES which determine the efficiency of the bio-diesel to be used as alternative source of fuel.

The FTIR analysis reveals the characteristic peaks on a bio-diesel spectrum are one at 1000-1300 cm^{-1} which is related to O-CH₃ vibrations. Comparing Figs. 5-8 shows that the peak characterized by O-CH₃ vibrations is prominent in all spectra. The peak gives an indication of the attachment of the alkali group of the alcohol to

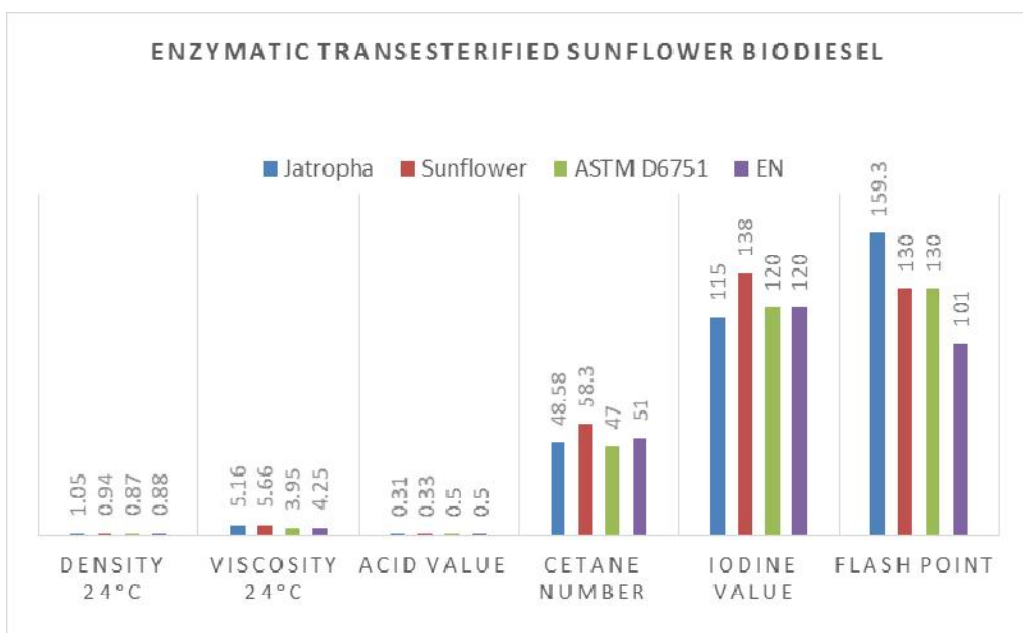


Fig. 4. Physico-chemical properties of sunflower bio-diesel produced by enzymatic transesterification, in comparison with jatropha bio-diesel, EN and ASTM standards

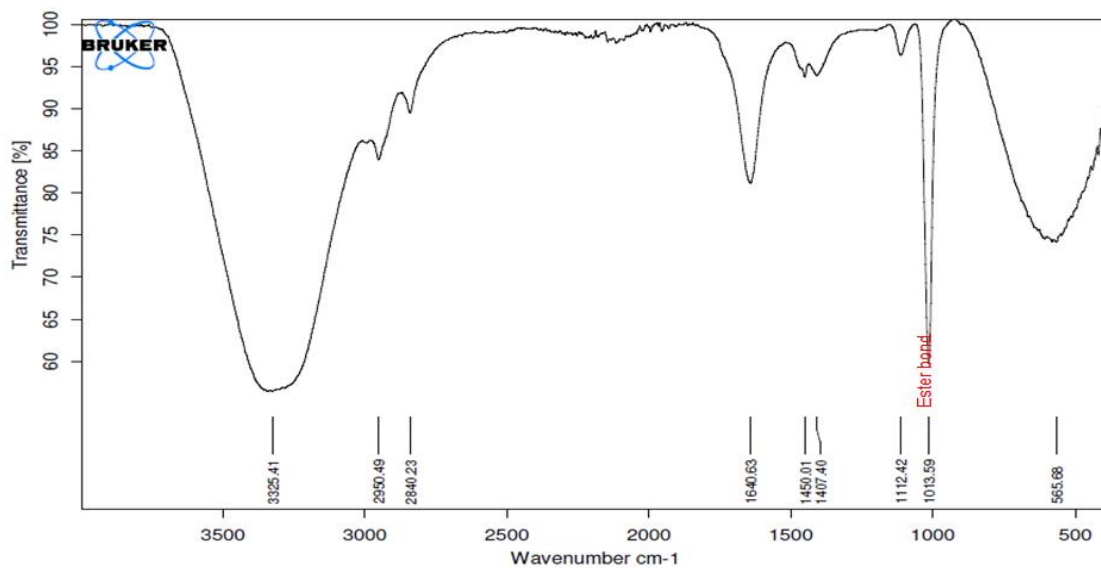


Fig. 5. FTIR spectrum of sunflower bio-diesel, obtained by acidic trans-esterification process for FAME's analysis

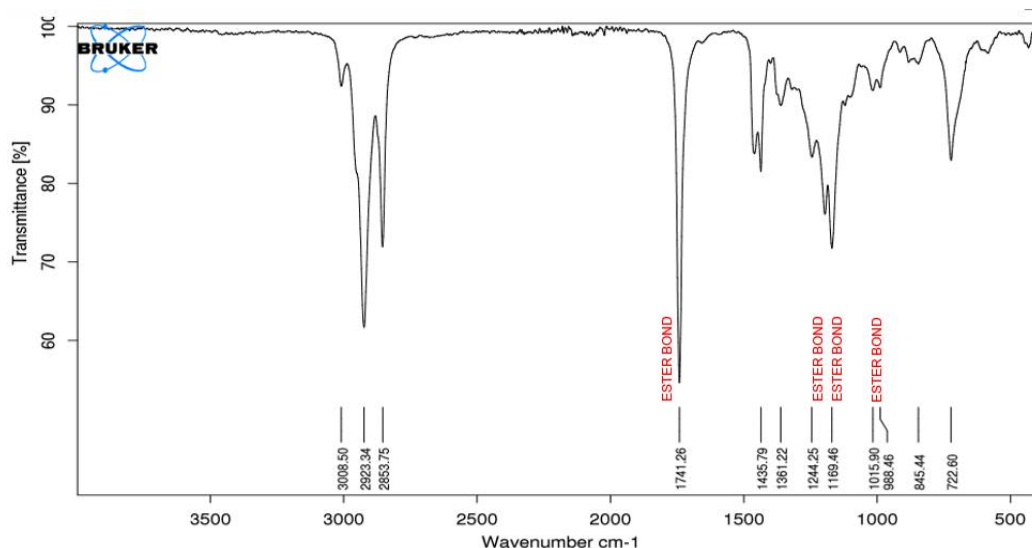


Fig. 6. FTIR spectrum of sunflower bio-diesel, obtained by from alkaline trans-esterification process for FAME's analysis

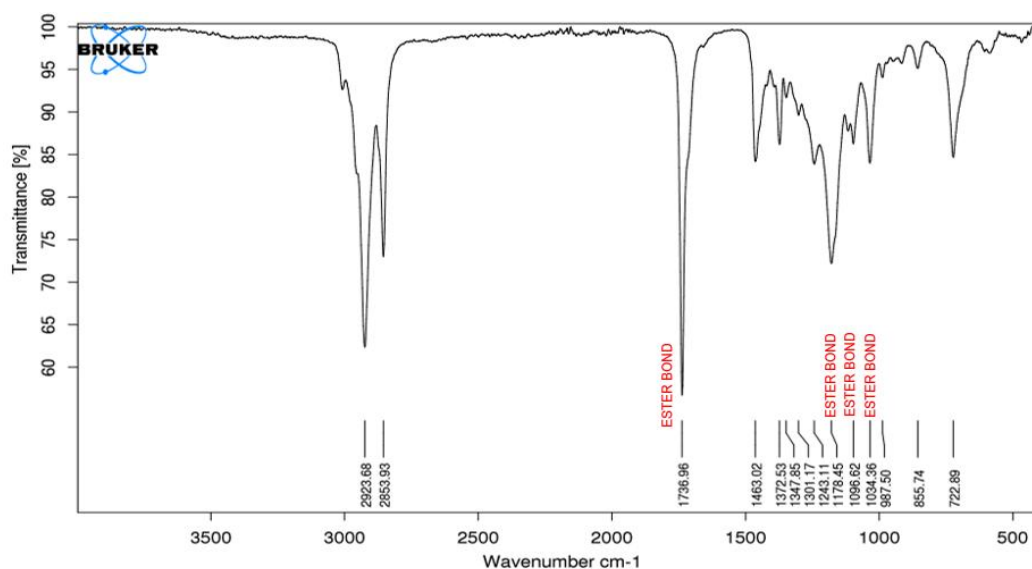


Fig. 7. FTIR spectrum of sunflower bio-diesel, obtained by from enzymatic trans-esterification process for FAME's analysis

the fatty acid group in the triglycerides, those forming esters. In addition there are bonds appearing between 1150-1450 cm^{-1} attribute to C-O ester stretching vibrations and 1735-1750 cm^{-1} both attribute to C=O ester stretching vibrations. 1000-1400 cm^{-1} attribute to alkyl halide C-F stretching vibrations, 1080-1360 cm^{-1} attribute to amine group C-N stretching vibrations, 2850-3000 cm^{-1} attribute to alkanes C-H stretching vibrations, 1720-1740 cm^{-1} attribute to aldehyde group C=O stretching

vibrations, 1670-1820 cm^{-1} attributes to ester carbonyl C=O stretching vibrations, 2500-3300 cm^{-1} attributes to acid group O-H stretching vibrations and 1400-1600 cm^{-1} attributes to aromatic groups C=C stretching vibrations. The analysis confirms the purity of the respective bio-diesel samples with the presence of methyl ester groups. Thus presence of FAMES plays an important role in determining the bio-diesel efficiency.

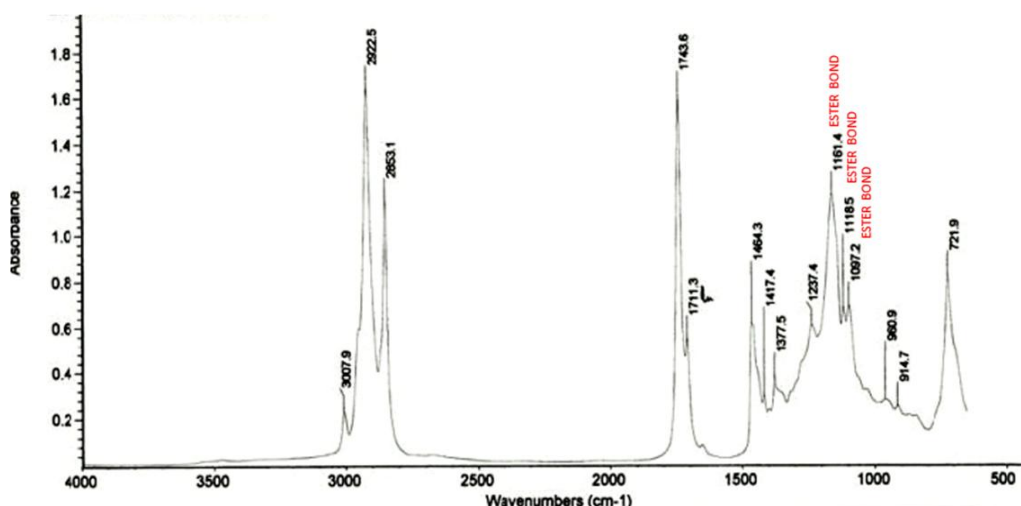


Fig. 8. FTIR spectrum of jatropha bio-diesel, obtained by from enzymatic trans-esterification process for FAME's analysis (used as comparative standard)

From the above obtained FTIR peaks, sunflower bio-diesel from alkaline and enzymatic method were found to be effective with the presence of good amount of methylesters when compared with the acidic method. Whereas, alkaline method is cost effective and easy to handle process and enzymatic method is time consuming. Thus alkaline method holds the suitable method.

The fatty acid methylesters are the key parameter to denote the bio-fuel efficiency [30]. Based on the FAMEs analysis (Figs. 5-8) the bio-diesel obtained from alkaline method and enzymatic method had good amount of fatty acid esters and was found to be similar with standard jatropha bio-diesel. Bio-diesel obtained by these methods has the potential to be used as an alternative source of fuel in the form of blends. Alkaline method is cost effective and easily produced whereas the enzymatic method is costly and requires longer duration for bio-diesel production. However acid method was found to contain the least amount of FAMEs and is not efficient to be used as bio-fuel as it does not meet the standard criteria's.

4. CONCLUSION

The bio-diesel obtained by alkaline trans-esterification of residual sunflower oil by virtue of more fatty acid methyl ester content and other physico-chemical properties showed as better alternative with good fuel efficiency in terms of cetane number. This bio-diesel has the capability

to act as an alternative fuel to jatropha bio-diesel used as blends. The production of bio-diesel from residual sunflower oil minimizes the environmental oil dumps that cause soil and water pollution. Further, it lays a foundation for the further research to be carried on for optimal use as an alternative fuel.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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